Effects of electronic correlation on X-Ray absorption and dichroic spectra at L$_{2,3}$ edge

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We present a new theoretical approach to describe X-Ray absorption and Magnetic Circular Dichroism spectra in the presence of e-e correlation. Our approach provides an unified picture to include correlations in both charged and neutral excitations, namely in direct / inversion photoemission where electrons are removed/added, and photo absorption where electrons are promoted from core levels to empty states. We apply this approach to the prototypical case of L$_{2,3}$ edge of $3d$ transition metals and we show that the inclusion of many body effects in the core level excitations is essential to reproduce, together with satellite structures in core level photoemission, the observed asymmetric line shapes in X-ray absorption and dichroic spectra.

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The excitation due to X-ray absorption is a complex phenomenon where many body effects may play a major role. The independent particle picture has been shown to be inadequate in describing features of X-ray absorption spectra in transition metals[1] and their compounds[2,3] where e-e interactions are known to be non negligible. To account for these failures various theoretical methods have been developed that differ on how the e-e Coulomb interaction is taken into account. They range from atomistic approaches, where a parameterized many body Hamiltonian is solved via configuration interaction methods[2], to solid state first-principles schemes that include properly the structure of valence electrons[4,5] but loose some of the atomic many-body effects that can be relevant to the physics of the process.

In this paper we present a new approach that treats on the same footing the localized and itinerant character of electrons in a solid, exploiting on one side the first principle calculations of the band structure and on the other side the localized picture to treat many body effects associated to electron-electron interactions. We will show that the on-site interaction between core and valence electrons, responsible of satellite structures in core level photoemission spectra, gives rise to asymmetric line shapes in XAS and XMCD spectra in agreement with experiments. Application to the prototypical case of absorption from the $L_{2,3}$ edge in $3d$ transition metals is presented.

Within the independent-particle scheme the X-ray absorption is described as the addition of one electron-hole pair to a non-interacting Fermi sea. In the language of many-body theory, this corresponds to approximate the two-particle polarization propagator to zeroth order. It is possible to improve this approach by substituting the bare particle and hole propagators with the dressed ones. Except for vertex corrections this would be the *exact* two-particle propagator. This picture is very physical in the sense that the creation of the e-h pair due to X-ray absorption can be visualized as the removal of one core electron in the presence of the valence continuum and its addition to the conduction band, a sort of superposition of photoemission and inverse photoemission spectra, plus possible electron-hole interaction.

Even neglecting the excitonic effects associated to the electron-hole interaction we are left with a very hard task, namely the calculation of hole and particle propagators of an interacting many particle system. This is even more difficult here since we are dealing with two processes that from the point of view of e-e interactions are very different: on one side the removal of one electron from an inner core state with atomistic interactions resulting in multiplet structures that in most cases survive the band formation; on the other side the addition of one electron in an itinerant conduction state where local short range e-e interactions coexist with hopping from site to site. An approach that can treat these two apparently opposite situations in an unique way is based on the generalized Hubbard model where the different strength of localization can be taken into account in terms of different U and J parameters and different band widths (finite and zero band width for valence states and non-dispersive inner core energy levels respectively). In the present case the Hubbard Hamiltonian can be usefully partitioned in core (c) and valence (v) contributions

$$\hat{H} = \hat{H}_v + \hat{H}_c. \qquad (1)$$

The first term describes valence states in terms of single particle band eigenvalues ($\epsilon_{kn\sigma}$) and of on-site Coulomb (U_{vv}) and exchange (J_{vv}) interaction

$$\hat{H}_v = \sum_{kn\sigma} \epsilon_{kn\sigma}\hat{n}_{kn\sigma} + \frac{1}{2}\sum_{i\sigma\sigma'}(U_{vv} - J_{vv}\delta_{\sigma\sigma'})\hat{n}_{iv\sigma}\hat{n}_{iv\sigma'}$$

Here i is the site index. Similarly

$$\hat{H}_c = \hat{H}_{cc} + \hat{H}_{cv}$$

where

$$\hat{H}_{cc} = \sum_{i\sigma}[\epsilon_{c\sigma}\hat{n}_{ic\sigma} + U_{cc}\hat{n}_{ic\sigma}\hat{n}_{ic-\sigma}]$$

$$\hat{H}_{cv} = \frac{1}{2} \sum_{kk'p} \sum_{\sigma\sigma'} (U_{cv} - J_{cv}\delta_{\sigma\sigma'}) C^{n*}_{k'\sigma'} C^{n}_{k'-p\sigma'} \quad (2)$$
$$\times \; \hat{a}^{c\dagger}_{k\sigma} \hat{a}^{c}_{k+p\sigma} \hat{a}^{n\dagger}_{k'\sigma'} \hat{a}^{n}_{k'-p\sigma'}.$$

Notice that $\hat{H}_c$ includes both core-core (U_{cc}) and core-valence (U_{cv},J_{cv}) e-e interaction. In the present case we are interested in $L_{2,3}$ edge excitations, therefore we will consider Coulomb and exchange integrals involving $2p$ and $3d$ orbitals.

The orbital character of the valence band comes into our scheme through the d orbital coefficients $C^{n}_\sigma(k)$ of eq. 2 obtained in our case by ab-initio band structure calculation. Both core and valence states have been calculated within the full-potential, linearized plane-wave method (FLAPW) as implemented in the WIEN2K code[6]. Spin-orbit coupling has been included in order to reproduce a non-zero total orbital momentum that is one of the quantities that can be extracted from dichroic spectra. For core states the relativistic effects are accounted for by solving the Dirac equation while for valence states the spin-orbit coupling is treated by perturbation theory[7].

The ab-initio band structure results could also be used to estimate the U and J parameters: the bare on-site valence - valence and core - valence coulomb and exchange interactions can be explicitly calculated using the core and valence wavefunctions and properly scaled to account for screening effects. This procedure has been applied to the evaluation of core-core integrals in transition metals oxides assuming a static effective dielectric constant[8]. Various ab-initio estimate of on-site valence-valence Coulomb and exchange integrals have been recently proposed for $3d$ transition metals, either within a constrained density functional approach[9] or as dynamicaly screened on-site integrals[10]. The results depend on the procedure adopted and the range of variation in the parameters (1 to 5 eV) remains the same reported previously in the literature[11]. In the present calculation U and J have been used as adjustable parameters, with values for valence-valence within the above mentioned range, tuned to optimize the agreement between theory and experiment. Their values are reported in table I. These values for the valence-valence interactions give an accurate description of the quasiparticle band dispersion probed by angular resolved photoemission[12–14]. The same is true of core-core interactions that have been fixed to reproduce the satellite position in core level photoemission spectra (see next figure on core level photoemission).

When dealing with charged excitations where one electron is removed from a core level or added to an empty valence state one can solve independently $\hat{H}_c$ or $\hat{H}_v$ to obtain hole and particle spectral functions respectively. This is done here using the 3-body scattering (3BS) approach that has been implemented to treat both core and valence spectra[8,14–16]: a charged excitation is described in terms of scattering between the single particle state with one removed/added particle and the excited configurations containing one extra e-h pair.

Energy and spin dependent complex self-energies

TABLE I: Coulomb and exchange integrals (in eV) describing the interaction between valence ($3d$) and core ($2p$) states.

	U_{dd}	J_{dd}	U_{pd}	J_{pd}
Fe	1.5	0.9	0.8	0.1
Co	2.1	0.9	1.8	0.2
Ni	2.0	0.9	2.5	0.2

$\Sigma^{c/v}_\sigma(\omega)$ are calculated and from them spectral functions for core and valence states given by

$$A^{c/v}_\sigma(\omega) = \frac{1}{\pi} Im \frac{1}{\omega - \epsilon^{c/v}_\sigma - \Sigma^{c/v}_\sigma(\omega)} \quad (3)$$

Please notice that for valence states the spectral function depends on band index and k-vector: $A^{v}_\sigma(\omega) \equiv A_{kn\sigma}(\omega)$ the k- and band index dependence coming from $\epsilon^v \equiv \epsilon_{kn}$ and possibly from the self-energy.

Let us start from the core hole excitation. Within the present approach the hole self energy turns out to be[14,16]

$$\Sigma^{c}_\sigma(\omega) = \int_{E_F}^{+\infty} n_{d-\sigma}(\epsilon)[U_{cv} - T^{cv}_{hh}(\omega-\epsilon) \cdot$$
$$\cdot (1 + U_{cv}A_{cd}(\omega-\epsilon))]d\epsilon$$
$$+ \int_{E_F}^{+\infty} n_{d\sigma}(\epsilon)[(U_{cv} - J_{cd}) - \tilde{T}^{cv}_{hh}(\omega-\epsilon) \cdot$$
$$\cdot [1 + (U_{cv} - J_{cv})]\tilde{A}_{cd}(\omega-\epsilon)d\epsilon. \quad (4)$$

Here $n_{d\sigma}(\epsilon)$ is the d contribution to the valence density of states of spin σ. The hole-hole scattering associated to the on-site interactions is described by T-matrices T^{cv}_{hh} and $\tilde{T}^{cv}_{hh}$ for scattering between antiparallel and parallel spin holes respectively; similarly A_σ ($\widetilde{A_\sigma}$) includes antiparallel (parallel) electron-hole scattering[16].

Fig. 1 shows the calculated spectral functions for the $2p$ core level of Fe, Co and Ni obtained assuming the U and J values of table I with binding energies adjusted to the experimental values[17]. Since our calculated self-energy is responsible of an intrinsic broadening identical at the two edges, to reproduce the observed different lifetimes at the two edges we have added extra broadening $\delta = 0.5eV$ and , $\delta = 1.5eV$ for $2p_3/2$ and $2p_2/2$ respectively. The spectral functions reproduce the essential features of the core photoemission data for transition metals where a main peak is always followed by a satellite structure at higher binding energies. This structure is the fingerprint of e-e correlation being commonly attributed to the admixture of different single particle configurations: not just the ground state with one core electron missing but also the shake-up states where electrons are promoted to higher energy levels. These physical processes are contained in our many body description based, as previously mentioned, on an extension to the solid state of the configuration interaction scheme.
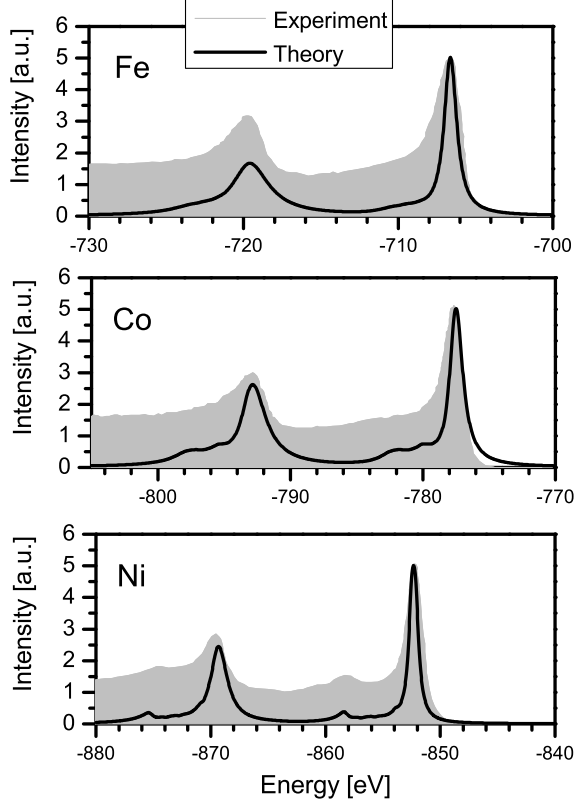
FIG. 1: 2P core level photoemission for Fe, Co and Ni inclusive of correlation effects (black line) compared with experimental ones[17] (grey area).
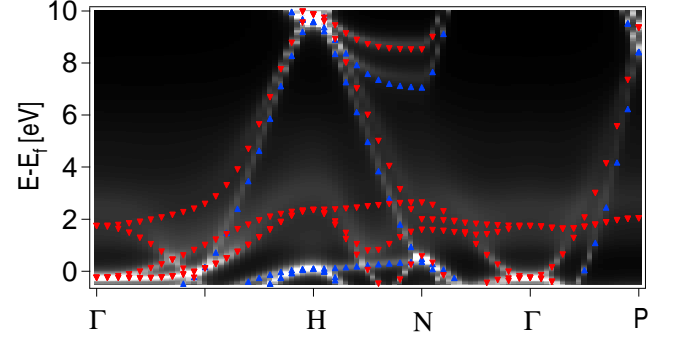

FIG. 2: (color online) Iron empty states: interacting spectral functions are shown as color map and compared with single particle eigenstates reported as red (spin down) and blu (spin up) arrows. In this energy region self-energy corrections for majority spin states are negligible.

dipole matrix elements

$$\mu_0^{\pm}(\omega) \propto \sum_{kn} |D_{ckn}^{\pm}|^2 \sum_{\sigma} Im\chi_{ckn\sigma}^0(\omega) \qquad (5)$$

with

$$Im\chi_{ckn\sigma}^0(\omega) = \int_{-\infty}^{\infty} \delta(\Omega - \epsilon_{c\sigma})\delta(\omega + \Omega - \epsilon_{kn\sigma})d\Omega$$

One effect of many body correlation is to replace this joint density of states with the convolution of hole and particle spectral functions. Formally this corresponds to calculate a two-particle polarization propagator $\chi_{cv}(\omega)$ where the bare particle and hole propagators are substituted with the dressed ones

$$\mu^{\pm}(\omega) \propto \sum_{kn} |D_{ckn}^{\pm}|^2 \sum_{\sigma} Im\chi_{ckn\sigma}(\omega) \qquad (6)$$

with

$$Im\chi_{ckn\sigma}(\omega) = \int A_{\sigma}^c(\Omega)A_{kn\sigma}(\Omega + \omega)d\Omega$$

$D_{ckn}^{\pm}$ appearing both in eq. (5) and eq. (6) is the matrix element of the electric dipole moment over the core and valence states

$$D_{ckn}^{\pm} = \sum_{m_j=-j}^{j} \langle \Psi_{jm_j}^c |\hat{\epsilon}^{\pm} \cdot e \; \mathbf{r} \; |\Psi_{kn}\rangle \qquad (7)$$

with $\hat{\epsilon}^{\pm}$ the polarization vector (left/right) of the incident photon, e the electron charge, $\Psi_{jm_j}^c$ and Ψ_{kn} the spin-orbit split core and valence eigenstates respectively.. The XMCD signal is obtained as the difference $\mu^+(\omega)-\mu^-(\omega)$.

Figure 3 shows the calculated absorption (a) and dichroic (b) spectra for Fe, Co and Ni calculated both with and without self-energy corrections, compared with

We turn now to valence states. The self-energy correction to a valence band level $\epsilon_{kn\sigma}$ is slightly more complicated with respect to the core one reflecting the complex valence band structure where different orbitals are inextricably hybridized (for a detailed description of the valence self-energy see reference[14]).

The effect of correlation on empty states is shown in figure 2 for iron where the electron spectral functions are shown along high symmetry directions of the Brillouin zone. Notice that only some of the empty bands (the minority spin ones of d orbital character) are affected by self-energy corrections, mainly in terms of life time broadening. The overall effect of correlation on empty states is however very small, and even smaller for Cobalt and Nickel where d states are almost fully occupied.

The response of interacting electrons to the creation of an e-h pair due to X-ray absorption is connected to these hole and particle spectral functions: within the single particle approach the absorption cross section is just the joint density of core and valence states modulated by the

experimental data[18,19]. We notice that in most cases the inclusion of many-body effects improves the agreement with experimental XAS spectra, making the lines more asymmetric. What makes line shapes asymmetric is the presence of shake-up satellite structures in the hole-spectral functions. These structures are essential to recover asymmetric line shapes also in XMCD spectra. Since in our calculation the L_2 and L_3 lines have the same line shape by construction, the only difference being their width, it is not surprising that the asymmetry in the dichroic lines is the same at the two edges. In the case of nickel where both peaks in the measured dichroic spectrum present the same pronounced asymmetry, the inclusion of e-e correlation improves the agreement between theory and experiment. For iron and cobalt on the contrary we are able to reproduce rather well the dichroic line shape at the L_2 edge but less accurately the L_3 one which turns out to be experimentally rather symmetric and more similar to the uncorrelated result. The asymmetry of the L_2 edges increases from Fe to Ni, in agreement with the corresponding trend in the core-valence electronic correlation described by U_{pd} (see Tab. 1).

As we mentioned at the beginning what is still missing in this description is the e-h attraction responsible of excitonic effects. These effects can be included by considering the two-particle eigenvalue problem assuming the excited states of the N-particle interacting system to be a superposition of single particle states with one core hole and an electron above the Fermi level. This is the so-called Tamm-Dancoff approximation (TDA)[20] and is at the core also of the 3BS scheme applied here to describe the charged excitations - just one e-h pair added in this case to the $N \pm 1$ -particle interacting system. TDA has been used to solve the Bethe-Salpeter equation (BSE) and treat excitonic effects in valence-valence transitions[21] and more recently extended to X-ray absorption from core states[5,22]. In both cases the dressed one-particle propagators have been obtained within the GW approximation[23]. In the present case we are interested in a regime of high e-e correlation where the a perturbative approach like GW is supposed to be less appropriate being unable to reproduce satellite structures that dominate the core level spectra. A non-perturbative method such as the 3BS approach would be more appropriate and we are presently testing the extension of our theory in this direction.

A further difference between the present approach and the ab-initio methods based on either GW+BSE[5,22] or time-dependent local density approximation[1] is the treatment of the e-e interaction: in these schemes the electrons interact through the full long range, dynamically screened Coulomb potential while in our approach only the short-range part of the Coulomb interaction is considered, in the spirit of the Hubbard model. The implicit assumption, common to most approaches used to describe e-e correlation in strongly correlated materials, is to attribute many body effects to just the on-site interaction,
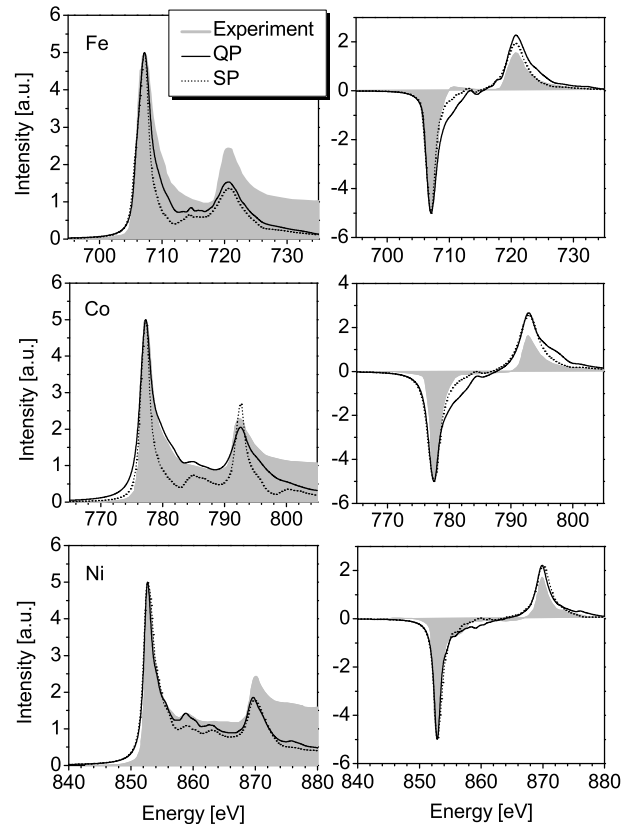

FIG. 3: Absorption (left panels) and dichroic(right panels) spectra of Fe, Co, Ni. Theoretical spectra, with (QP) and without (SP) self-energy corrections are compared with experimental ones[18,19] represented by gray areas.

the long range part being included at the mean-field level in the band calculation. This assumption seems particularly reasonable in the case of the strongly localized core states but in practice leads to the introduction of adjustable parameters. This is has been up to now a shortcoming of most the approaches based on the Hubbard model, with the advantage to allow for solutions beyond the perturbation limit.

In summary, we have shown that many-body effects due to e-e interactions can be included in the description of X-ray absorption and dichroic spectra by replacing the joint density of states appearing in the absorption cross-section with a convolution of (core) hole and (valence) electron spectral functions. Whenever e-e correlations modify significantly hole and electron spectral functions we expect non negligible effects in the absorption spectra as well. In the case of $3d$ transition metals these modifications are essentially associated to the shake-up structures that appear in the core-level photoemission spectra as a residue of atomic multiplets. These structures, related to

the admixture of different single particle configurations, can be reproduced only in a many body approach and are responsible of the asymmetric line shapes of XAS and XMCD structrues at L$_{2,3}$ edges in Fe, Co and Ni. In other systems where local e-e correlations affect significantly the empty part of the valence band we expect even more drastic changes: this should be the case for instance of highly correlated materials where on site e-e repulsion is responsible of the creation of extra empty (Hubbard) bands[24].

Finally we want to stress that our approach has a purely experimental counterpart: it would be interesting to check on an experimental basis wether - and to what extent - the measured absorption spectra can be re-

produced as a straightforward convolution of direct and inverse photoemission data, in this way confirming the direct link between neutral excitations, due to X-ray absorption, and charged excitations corresponding to hole and electron addition, link that is clear theoretically but that has not been demonstrated experimentally so far.

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